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PATENT SPECIFICATION

NO DRAWINGS

1,170,300



1,170,300

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COMPLETE SPECIFICATION

Process for the manufacture of Elastomeric Polymers

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister, Lucius & Brüning, a body corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to elastomeric block polyether amides and block polyester amides and a process for their manufacture.

Various processes are known for making polyether amides and polyester amides. Polyester amides are obtained, for example, by incorporating amino alcohols, diamines or dicarboxylic or hydroxycarboxylic acids containing amide groups into polyesters by condensation reactions at elevated temperatures in the presence of catalysts. Polyester amides are also obtainable from polycarboxylic acid anhydrides and cyclic urethanes, from dicarboxylic acid chlorides, glycols and diamines or from N,N'-acyl - bis- $\beta$ -lactams and glycols or bisphenols.

The polyether amides and polyester amides hitherto known have possessed only the mixed properties of pure polyethers or polyesters and pure polyamides because the amide and ether or ester functions are statistically distributed in the chain molecules. When, for example, dicarboxylic acids containing amide groups are used, only polymers with statistically distributed ester and amide functions are obtained because of ester-interchange and transamidation which take place under the conditions of the polyester condensation. But even under conditions excluding ester-interchange and transamidation such components containing amide groups (all products hitherto known contain at most two amide groups) do not yield products with new properties since the components used are too short to have any influence as blocks in the molecule.

It is known from the chemistry of polyurethanes, however, that block polyester or polyether urethane ureas have new and valuable properties compared with statistical copolymers. These block polymers, which are elastomers of the so-called Spandex type, constitute heat-setting, elastic products, the properties of which are in many cases superior to those of conventional rubber. Their manufacture has been described, for example, in U.S. Patents 2,929,804 and 2,957,852. U.S. Patents 2,957,852 and 2,813,776 also describe, inter alia, the manufacture of polyesters and polyglycols having terminal carboxylic acid chloride groups.

This invention is based on the observation that elastomeric block polyether amides and polyester amides can be obtained by reacting polyether and/or polyester dicarboxylic or disulphonic acid halides having an average molecular weight within the range of 500 to 5,000 and a softening point below 60°C, if desired in admixture with up to 400 mol %, calculated on the amount of polyether and/or polyester dicarboxylic or disulphonic acid halide, of simple dicarboxylic acid halides, with oligoamides having a molecular weight of at least 230 and carrying terminal groups capable of being acylated, in an amount within the range of 10 to 50% by weight, calculated on the total weight of the starting substances, in the presence of acid-binding substances. The reaction is preferably carried out in solution, but may be carried out in substance.

As polyether and polyester dicarboxylic and disulphonic acid halides as well as

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the simple dicarboxylic acid halides there are preferably used the bromides and, advantageously, the chlorides. The polyether or polyester dicarboxylic or disulphonic acid halides of an average molecular weight within the range of 500 and 5,000, to be used in the process of the invention can be obtained in the following manner (the compounds referring to the preparation of the disulphonic acid halide being bracketed):

(a) reaction of polyethers or polyesters containing terminal hydroxyl groups with at least 2 moles of a dicarboxylic acid [disulphonic acid] halide or phosgene or with from 1 to 2 moles of a dicarboxylic acid [disulphonic acid] halide or phosgene, if a simultaneous chain lengthening is required;

(b) reaction of polyethers or polyesters containing terminal carboxyl [sulphonic acid] groups with halogenating compounds, for example, phosgene, thionyl chloride, phosphorus oxychloride, phosphorus pentachloride, phosphorus trichloride or the corresponding bromides.

Polyethers suitable for the manufacture of the polyether dicarboxylic or disulphonic acid halides are, for example, polyethylene oxide glycol, polypropylene oxide glycol, polytetramethylene oxide glycol, polypentamethylene oxide glycol, polyhexamethylene oxide glycol, polydecamethylene oxide glycol, polyisobutylene oxide glycol, poly - 1,2 - butylene oxide glycol; copolyethers of ethylene oxide and tetrahydrofuran, of propylene oxide and tetrahydrofuran or of tetrahydrofuran or propylene oxide and glycidyl ethers (preferably methyl and ethyl), glycidic acid esters (preferably methyl and ethyl), or epichlorhydrin, the preferred molar ratio in the copolyethers being within the range of from 1:2 to 2:1; bis - carboxymethyl derivatives of polyalkylene oxides, for example, HOOC - CH<sub>2</sub> (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub> OCH<sub>2</sub> - COOH and formals obtained, for example, from the reaction between hexamethylene glycol or pentamethylene glycol and formaldehyde. Some chain members in the polyethers or copolyethers may be aromatic or cycloaliphatic radicals. For example, *p*-xylene bromide may be reacted in an alkaline medium with polytetramethylene oxide glycol to yield polyethers having one or more xylylene radicals in the chain. The oxygen atoms of the polyethers may be partially replaced by sulphur atoms. A macro-glycol of this type can be obtained, for example, by splitting off water from a mixture of 1,4-butanediol and bis-hydroxyethyl thioether.

Polyesters suitable for the manufacture of the polyester dicarboxylic or disulphonic acid halides may be prepared, for example, from the following acids and diols: carbonic acid, oxalic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, pimelic acid, diglycolic acid, phthalic acid, isophthalic acid, terephthalic acid, hexahydroterephthalic acid, thiobutyric acid, ethylene glycol, di-, tri- or polyethylene glycol, 1,2- or 1,3 - propanediol, 1,4- or 2,3- or 1,3 - butanediol, 1,6 - hexanediol, 1,10-decanediol, 1,12 - octadecanediol, 2,2 - dimethyl - propanediol - (1,3), glycerol-monomethyl ether, N - bis - ( $\beta$  - hydroxyethyl) - aniline, and cyclohexylene glycol.

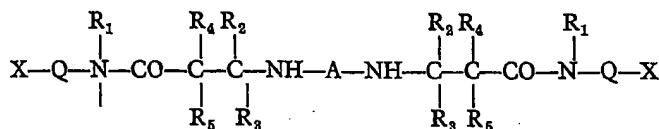
As condensates having molecular weights within the range of 500 to 5,000 but softening points of below 60°C, it is advantageous to use copolymers, for example, of adipic acid, ethylene glycol and 1,3 - butanediol, of adipic acid, phthalic acid and ethylene glycol or of terephthalic acid, ethylene glycol and polyethylene oxide glycol.

For the reaction of the polyethers or polyesters containing terminal hydroxyl groups with acid halides there may be used, for example, the acid halides of the following acids: carbonic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, isophthalic acid, terephthalic acid, hexahydroterephthalic acid, 4,4' - diphenylmethane dicarboxylic acid, 1,2 - ethanesulphonic acid, 1,6 - hexanedisulphonic acid, 1,5 - naphthalenedisulphonic acid, 1,3-benzenedisulphonic acid and 1,4 - benzenedisulphonic acid. Advantageously, sebacic acid is used.

The halides of the aforesaid acids may also be used in the form of simple dicarboxylic acid halides which are added, if desired, to the polyether and/or polyester dicarboxylic or disulphonic acid halides in an amount of up to 400 mol %, calculated on the amount of the polyether and/or polyester dicarboxylic or disulphonic acid halides.

The oligoamides containing terminal groups capable of being acylated, which are used in the process of the invention are advantageously obtained by transamidation of N,N' - acyl - bis - lactams and compounds capable of being bis-acylated in which one of the groups capable of being acylated is a primary or a secondary amino group.

When N,N' - acyl - bis -  $\beta$  - lactams are used as N,N' - acyl - bis - lactams, the transamidation proceeds substantially in one direction because of the strain in the four-membered ring. Oligoamides capable of being bisacylated and corresponding to the following general formula are obtained:



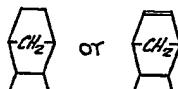
In the above formula, A represents the radical obtained by the removal of 2 OH groups from a dicarboxylic or disulphonic acid, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, isophthalic acid, terephthalic acid, hexahydroterephthalic acid, 4,4' - diphenylmethane - dicarboxylic acid, 1,2 - ethanedisulphonic acid, 1,6 - hexane - disulphonic acid, 1,5 - naphthalenedisulphonic acid, 1,3 - benzenedisulphonic acid and 1,4 - benzenedisulphonic acid; or from a dicarboxylic or disulphonic acid which already contains amide, ester, ether or sulphonic groups, for example, N,N' - adipoyl - bis - p - aminobenzoic acid, 4 - carboxy - phenyl - oxamide acid, N,N' - terephthaloyl - bis - ε - aminocaproic acid, ethylene diamine - N,N' - diadicic acid, N,N' - di - δ - carboxylic - valeroylpiperazine, N,N' - p - xylylenediamine - dioxalic acid, diglycolic acid, 4,4' - diphenylether - dicarboxylic acid, or bis - (4 - carboxyphenyl) - sulphone. Of the above acids, oxalic acid and terephthalic acid are especially advantageous.

The group X-Q-N stands for the radical obtained by the removal of a H atom from the N atom of a compound capable of being bisacylated in which one of the groups capable of being acylated is a primary or secondary amino group of the R, formula  $\text{—N}^{\text{H}}<\text{—}$  and the other group X capable of being acylated is NH-R, OH, SH, or  $\text{SO}_2\text{NH—R}$ , the radicals R and R<sub>1</sub> which may be the same or different each representing an alkyl, alkenyl, cycloalkyl, aryl or aralkyl group or a hydrogen atom and Q representing the rest of the molecule.

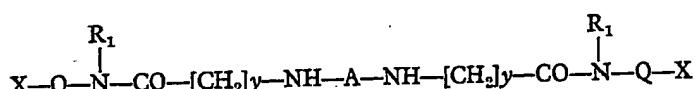
Examples of suitable compounds of the formula X-Q-N-H capable of being bisacylated are diamines, for example, ethylenediamine, tetramethylenediamine, hexamethylenediamine, N - methylmethylenediamine, N,N' - dimethylmethylenediamine, N - α - propylpropylenediamine - (1,3), 4 - aminobenzylamine, 3 - aminobenzylamine, p - xylylenediamine, β - (4 - aminophenyl) - ethylamine, γ - (3 - aminophenyl) - propylamine, m - phenylenediamine, p - phenyldiamine, 2,4 - toluylenediamine, benzidine, 4,4' - diaminodiphenylmethane, 4,4' - diaminodibenzyl, 2,4-diaminodiphenyl, 2,6 - diaminonaphthalene, piperazine, 3,3' - dichloro - 4,4' - diaminodiphenyl and 3,3' - dimethoxy - 4,4' - diaminodiphenyl, amino alcohols, for example, ethanolamine, 1 - amino - propanol - (2), 4 - hydroxybenzylamine, 4 - aminobenzyl alcohol, 1 - aminomethyl - 2 - naphthol, 4 - aminomethylbenzyl alcohol and 4 - aminomethyl - cyclohexyl - methanol, aminophenols, for example, and m- or p - aminophenol and m- or p - aminothiophenol, cysteamine, 4 - aminomethylbenzene - sulphonamide, compounds already containing amide, ester, ether or sulphonic groups, for example, glycolic acid - (2 - aminoethyl) - amide, ethylenediamine-N,N'-dioxalic acid - dihydrazide, ethylenediamine - N,N' - dioxalic acid - bis - (2-aminoethylamide), 4,4' - diaminodiphenyl ether, 4,4' - diaminodiphenylsulphone, glycine hydrazide, N - [4 - aminobenzoyl] - p - phenylenediamine, 4 - aminobenzoic acid - (4' - aminophenyl ester) and finally compounds containing no Q, for example, hydrazine, methyl - hydrazine, diethylhydrazine and hydroxylamine. We hereby disclaim any use of benzidine in contravention of the Carcinogenic Substances Regulations 1967 while these Regulations remain in force.

The radicals R<sub>1</sub> to R<sub>6</sub> which may be the same or different each represents an alkyl, alkenyl, cycloalkyl, aryl or aralkyl group or a hydrogen atom. Preferred radicals are H,  $\text{CH}_3$ ,  $\text{—C}_2\text{H}_5$ ,  $n\text{—C}_3\text{H}_7$ ,  $\text{—CH}=\text{CH}_2$ , cyclohexyl,  $\text{C}_6\text{H}_5$  and  $p\text{—C}_6\text{H}_4\text{—CH}_3$ .

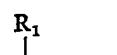
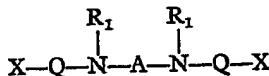
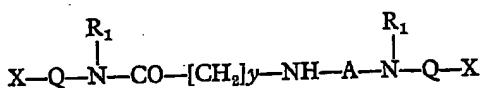
R<sub>2</sub> + R<sub>4</sub> and R<sub>3</sub> + R<sub>5</sub>, respectively, may form members of an aliphatic saturated or unsaturated ring. R<sub>2</sub> + R<sub>4</sub> and R<sub>3</sub> + R<sub>5</sub>, respectively, are advantageously



The transamidation of N,N' - acyl - bis - lactams of a larger number of ring members yields a mixture of three compounds of the following general formulae:



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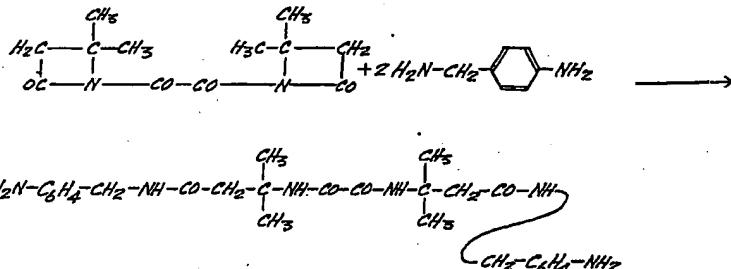
in which A and X-Q-N have the meanings given above and y is a whole number within the range of from 3 to 10.

The compounds are not separated and the mixture may be used as such for building up block polymers.

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The manufacture of oligoamides capable of being bisacylated by transamidation of N,N' - acyl - bis -  $\beta$  - lactams has already been described in French Patents 1,437,020 and 1,437,021. For an illustration there may be indicated the reaction of N,N' - oxalyl - bis - (4,4 - dimethylazetidine - 2 - one (with p - aminobenzylamine;

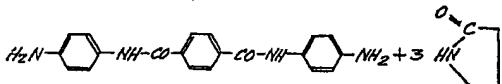
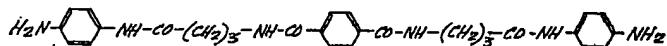
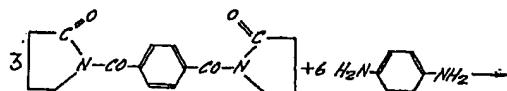
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and the reaction of N,N' - terephthaloyl - bis - pyrrolidone - 2 with p - phenylene-diamine:

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It is advantageous to use derivatives of  $\text{N},\text{N}'$  - acyl - bis -  $\beta$  - lactams (obtainable according to German Auslegeschrift 1,186,065), and preferably 4,4' - dimethylazetidinone, for the synthesis of the block polyether (ester) amides because of the specific nature of the reaction and the higher yields obtained as well as the high melting points of the reaction products.

When it is intended to obtain elastomeric block polyether (ester) amides for textile uses, oligoamides of high melting points are desirable. The softening points of the elastomers should be at least 150°C. The reaction of the polyether and/or polyester dicarboxylic or disulphonic acid halides with the oligoamides containing terminal groups capable of being acylated, is carried out according to the prescriptions used for acylations in the presence of acid-binding substances that is, substances that react with an acid to give a neutral compound. As acid-binding substances pyridine,  $\text{N}$ -methylpiperidine,  $\text{N},\text{N}$  - dimethyl aniline, triethylamine, sodium hydroxide, sodium carbonate and magnesium oxide may, for example, be used. When the reaction is carried out in solution, organic tertiary amines are preferred since they are soluble in the organic solvents used.

The reaction may be carried out in the absence of presence of a solvent. When working in the presence of solvents, it is advantageous to use those which dissolve the block polymer or at least swell it to a certain extent, for example, chlorobenzene, dioxane, acetonitrile, dimethylformamide, dimethylacetamide, phosphoric acid-tris-dimethylamide,  $\text{N}$  - methyl - pyrrolidone or mixtures of these solvents.

The reaction is preferably carried out at a relatively low temperature to avoid the occurrence of transacylations. The reaction temperature is therefore preferably within the range of -20 to +80°C, and advantageously within the range of 0 to +30°C. The time of reaction is preferably within the range of from 1 to 30 hours, advantageously between 5 and 10 hours. The reaction mixture is preferably stirred from time to time.

To obtain highly elastic products, an optimum ratio of polyether or polyester to oligoamide must be observed. Depending on the nature of the compounds used, the amount of oligoamide should be within the range of 10 to 50% by weight calculated on the total weight of the starting substances for the elastomer. When oligoamide components of low molecular weight are used, the said ratio is in general not obtained by using the substances in a molar ratio of 1:1.

A simple method of obtaining relatively high proportions of oligoamides consists in adding simple dicarboxylic acid halides to the polyether or polyester dicarboxylic acid halides and then to carry out the reaction using an increased amount of oligoamide. Especially when the polyether or polyester dicarboxylic acid halides are obtained by reacting polyethers or polyesters having terminal hydroxyl groups with dicarboxylic acid halides, it is advantageous to use from the beginning an excess amount, that is an amount corresponding larger than 2 moles, of dicarboxylic acid halide since this substantially prevents a chain lengthening of the polyether or polyester by a double reaction at the same dicarboxylic acid halide. For the same reason, the polyether or polyester containing terminal hydroxyl groups is preferably slowly added to the acid dihalide together with an acid-binding substance in order to ensure that the acid dihalide is always present in excess.

There may be cases, however, in which the molecular weight of the polyether or polyester is undesirably low. In this case, a deficiency, that is less than 2 moles, but more than 1 mole, of dicarboxylic acid halide is used per mole of polyether or polyester in the manufacture of the polyether or polyester containing terminal acid halide groups, in order to obtain a chain lengthening.

The second reaction stage is carried out in the same vessel. The oligoamide is added together with an acid-binding agent to the polyether or polyester containing terminal acid halide groups. When proceeding in the presence of a solvent, the salt which has been formed can generally be removed from the viscous solution by pressure filtration and the block polymer may be spun directly or may be precipitated.

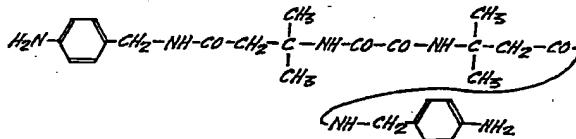
The properties of the elastomeric products can be modified within wide limits by an appropriate choice of the components and variation of the concentrations in which the components are used. For example, the softening points may be within the range of from room temperature to about 300°C, the elongation at break may vary between a few per cent and about 1500% and the solubility between good solubility and complete insolubility.

The products may be used, for example, for the manufacture of elastic heat-setting filaments, fibres, sheets and films or elastic shaped structures, as raw materials for lacquers and varnishes, or as adhesives and thickening agents.

The following Examples illustrate the invention. The parts are by weight, and the percentages referring to the solutions are also by weight. The spinning solutions and precipitating baths are at room temperature. By acid-number is meant the number of milligrams of KOH necessary to neutralize one gram of substance.

#### EXAMPLE 1

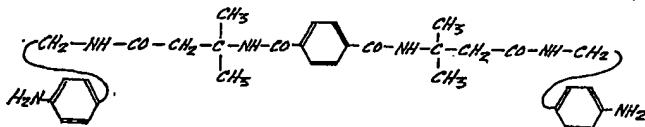
19.8 Parts of a copolyester of adipic acid, ethylene glycol and diethylene glycol ( $\approx 1:1$ ) with a content of hydroxyl groups of 1.61% and an acid number smaller than 1.5, were dissolved in 100 parts of N-methylpyrrolidone and 20 parts were distilled off to remove low boiling parts and water. After the addition of 1.82 parts of triethylamine, the solution was introduced within 20 minutes, while cooling with ice, into a solution of 8.6 parts of sebacinyl chloride in 30 parts of chlorobenzene. The batch was allowed to stand for 4 hours at room temperature. Then a solution of 13.41 parts of  $N,N'$ -oxaryl - bis - [ $\beta$  - amino - isovaleric acid - (4 - aminobenzyl) - amide] of the formula



(obtained from 1 mole of  $N,N'$ -oxaryl - bis - (4,4 - dimethylazetidine - 2 - one) and 2 moles of 4 - aminobenzylamine, melting point after crystallization from dimethylformamide 263°C), 6 parts of triethylamine and 100 parts of N-methylpyrrolidone was added within 20 minutes while cooling with ice. After reacting for some hours at room temperature, the precipitated triethylamine hydrochloride was removed from the viscous solution by pressure filtration, the chlorobenzene was drawn off at low temperature under reduced pressure and the product was precipitated with water or spun directly from the solution. There were obtained 39 parts of an elastomer having an oligoamide content of about 34%, a relative viscosity of  $\eta_{rel}$ . of 2.1, determined on a solution of 1 g of substance in 100 ml of  $\alpha$  - chlorophenol at 20°C, and a softening point of about 160°C. Filaments spun into water form a 50% solution in dimethylformamide had an elongation at break of 500% and an elastic recovery of 80% at an elongation of 100%.

#### EXAMPLE 2

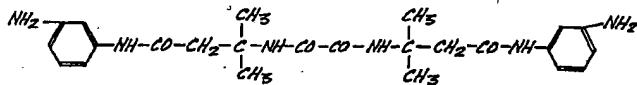
17.6 Parts of a copolyester of adipic acid, ethylene glycol and diethylene glycol ( $\approx 1:1$ ) having a content of hydroxyl groups of 1.61% and an acid number smaller than 1.5, were dissolved in 120 parts of N - methylpyrrolidone and 20 parts were distilled off to remove low-boiling parts and water. After the addition of 1.62 parts of triethylamine the solution was added within 30 minutes at 20°C to a solution of 7.31 parts of terephthaloyl chloride in 65 parts of chlorobenzene. The batch was heated at 40°C for 10 hours. Then a solution of 16.04 parts of  $N,N'$  - terephthaloyl - bis - [ $\beta$  - amino - isovaleric acid - (4 - aminobenzyl) - amide] of the formula



(obtained from 1 mole of  $N,N'$  - terephthaloyl - bis - (4,4 - dimethylazetidine - 2-one) and 2 moles of 4 - aminobenzylamine, melting point after crystallization from dimethylformamide  $223^{\circ}\text{C}$ ), 6.5 parts of triethylamine and 120 parts of  $N$  - methylpyrrolidone was added within 30 minutes at  $20^{\circ}\text{C}$ . The batch was reacted by heating for 5 hours at  $40^{\circ}\text{C}$ , the triethylamine hydrochloride was removed by pressure filtration at elevated temperature and after removal of the chlorobenzene the product was spun into water or precipitated with water. 38.4 Parts of an elastomer having a content of oligoamide of about 42%, a relative viscosity  $\eta_{\text{rel}}$  of 1.9, determined on a solution of 1 g of substance in 100 ml of  $\alpha$ -chlorophenol at  $20^{\circ}\text{C}$ , and a softening point of about  $190^{\circ}\text{C}$  were obtained in a substantially quantitative yield. Filaments spun into water from a 35% solution in dimethyl sulphoxide had an elongation at break of 340%, an elastic recovery of 85% at an elongation of 100% and a tensile strength of 0.5 g/den.

**EXAMPLE 3**  
20.4 Parts of a poly - 1,2 - butylene oxide glycol of an average molecular weight of 1020 were dissolved in 90 parts of  $N$  - methyl - pyrrolidone and 20 parts were distilled off to remove readily volatile parts and water. After the addition of 4.05 parts of triethylamine, the solution was added within 20 minutes, while cooling with ice, to a solution of 11.0 parts of sebacinyl chloride in 35 parts of chlorobenzene. The batch was allowed to stand for 4 hours at room temperature and a solution of 12.91 parts of  $N,N'$  - oxalyl - bis - [ $\beta$  - amino - iso - valeric acid - (4 - aminobenzyl) - amide], 6 parts of triethylamine and 100 parts of  $N$  - methylpyrrolidone was then added within 20 minutes while cooling with ice. After some hours at room temperature, the viscous solution was clarified by pressure filtration, the chlorobenzene was drawn off under reduced pressure and the polymer was precipitated with water. 40.5 Parts of an elastomer having a content of oligoamide of 31.5%, a relative viscosity  $\eta_{\text{rel}}$  of 2.1, determined on a solution of 1 g of substance in 100 ml of  $\alpha$ -chlorophenol at  $20^{\circ}\text{C}$ , and a softening point of about  $175^{\circ}\text{C}$  were obtained. Filaments spun into water from a 42.5% solution in dimethylformamide had an elongation at break of 450% and an elastic recovery of 85% at an elongation of 100%.

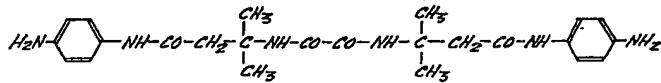
**EXAMPLE 4**  
24.24 Parts of a poly - 1,2 - butylene oxide glycol of an average molecular weight of 2020 were dissolved in 90 parts of  $N$  - methylpyrrolidone. 20 Parts of solvent were distilled off to remove slight amounts of moisture. After the addition of 2.43 parts of triethylamine, the solution was added within 20 minutes, while cooling with ice, to a solution of 8.8 parts of sebacinyl chloride in 35 parts of chlorobenzene. The batch was allowed to stand for 4 hours at room temperature. After that time a solution of 11.24 parts of  $N,N'$  - oxalyl - bis - [ $\beta$  - amino - isovaleric acid - (m - aminoanilide)] of the formula



(obtained from 1 mole of  $N,N'$  - oxalyl - bis - (4,4 - dimethylazetidine - 2 - one) and 2 moles of *p* - phenylenediamine, melting point after crystallization from dimethylamide/ethanol  $273^{\circ}\text{C}$ ), 6 parts of triethylamine and 100 parts of  $N$  - methylpyrrolidone was added within 20 minutes at 10 to  $15^{\circ}\text{C}$ . After reacting for some hours, the triethylamine hydrochloride was removed by pressure filtration, the chlorobenzene was drawn off under reduced pressure and the polymer was precipitated with water. 41 Parts of an elastomer having a content of oligoamide of 27%, a relative viscosity  $\eta_{\text{rel}}$  of 2.3, determined on a solution of 1 g of substance in 100 ml of  $\alpha$ -chlorophenol at  $20^{\circ}\text{C}$ , and a softening point of about  $160^{\circ}\text{C}$  were obtained. Filaments spun into water from a 45% solution in dimethylformamide had an elongation at break of 550%, an elastic recovery of 95% at elongation of 100% and a tensile strength of 0.6 g/den.

## EXAMPLE 5

32.32 Parts of an anhydrous poly - 1,2 - butylene oxide glycol of an average molecular weight of 2020 and 3.24 parts of triethylamine were dissolved in 130 parts of N-methylpyrrolidone. The solution was added within 20 minutes, while cooling with ice, to a solution of 8.6 parts of sebacic acid chloride in 30 parts of chlorobenzene. After 4 hours at room temperature, a second solution of 9.37 parts of N,N' - oxalyl - bis - [ $\beta$  - amino - isovaleric acid - ( $p$  - aminoanilide)] of the formula



(obtained from 1 mole of N,N' - oxalyl - bis - (4,4 - dimethylazetidine - 2 - one) and 2 moles of  $\psi$  - phenylenediamine, melting point after crystallization from dimethylformamide or pyridine 286°C), 4.55 parts of triethylamine and 140 parts of N-methyl - pyrrolidone was added within 20 minutes while cooling. The batch which rapidly became viscous was allowed to stand for some hours at room temperature. After pressure filtration and removal of the chlorobenzene the product was precipitated with water and dried at 60°C in a vacuum dryer. 47 Parts of an elastomer having a content of oligoamide of 19.6%, a relative viscosity  $\eta$  rel. of 2.0, determined on a solution of 1 g of product in 100 ml of *o*-chlorophenol at 20°C, and a softening point of about 225°C were obtained. Filaments spun into water from a 48% solution in dimethylformamide had an elongation at break of 580%, an elastic recovery of 97% at an elongation of 100% and a tensile strength of 0.4 g/den.

## EXAMPLE 6

26.25 Parts of a polypropylene oxide glycol of an average molecular weight of 1250 were dissolved in 120 parts of N - methylpyrrolidone. 20 Parts of the solution were distilled off to remove readily volatile parts. After the addition of 4.9 parts of pure triethylamine the solution was added within 20 minutes, while cooling with ice, to a solution of 12 parts of sebacinyl chloride in 40 parts of chlorobenzene. After the mixture had been allowed to stand for 4 hours at room temperature, a solution of 11.7 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - ( $p$  - aminoanilide)], 6 parts of triethylamine and 220 parts of N - methylpyrrolidone was added within 20 minutes while cooling with ice. After reacting for several hours at room temperature the triethylamine hydrochloride was removed from the viscous solution by pressure filtration, the chlorobenzene was drawn off and the elastomer was precipitated with water, washed and dried. 45 Parts of an elastomer having a content of oligoamide of 25.6%, a relative viscosity  $\eta$  rel. of 1.9, determined on a solution of 1 g of substance in 100 ml of *o*-chlorophenol at 20°C, and a softening point of about 230°C were obtained. Filaments spun into water from a 46% solution in dimethylformamide had an elongation at break of 300% and an elastic recovery of 90% at an elongation of 100%.

## EXAMPLE 7

27.36 Parts of a copolyether of tetrahydrofuran and ethylene oxide in a ratio of 1:1 of an average molecular weight of 910 were dissolved in 120 parts of N-methylpyrrolidone. 20 Parts were distilled off to remove moisture. After the addition of 7 parts of pure triethylamine, the solution was added dropwise within 20 minutes, while cooling with ice, to a cold solution of 12.65 parts of sebacinyl chloride in 30 parts of N-methylpyrrolidone. After 4 hours at room temperature, a second solution of 7.5 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - ( $p$  - aminoanilide)], 4 parts of triethylamine and 150 parts of N - methylpyrrolidone was added under the same conditions. The batch was allowed to stand overnight at room temperature, the elastomer was then precipitated with water, washed and dried. 41.5 Parts of a product having a content of oligoamide of 17.6%, a relative viscosity of  $\eta$  rel. of 1.7, determined on a solution of 1 g of polymer in 100 ml of *o*-chlorophenol at 20°C, and a softening point of about 220°C were obtained.

## EXAMPLE 8

31.5 Parts of a copolyether of tetrahydrofuran and propylene oxide in a ratio of 1:1, having an average molecular weight of 1260 were dissolved in 140 parts of N - methylpyrrolidone. 30 Parts of solvent were distilled off to remove moisture. After the addition of 5.82 parts of triethylamine, the solution was added dropwise

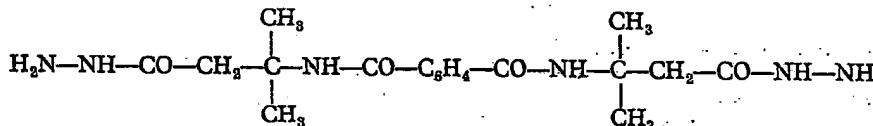
within 20 minutes, while cooling with ice, to a soluton of 11.85 parts of sebacinyl chloride in 40 parts of N-methylpyrrolidone. After 4 hours at room temperature, a second secolution of 8.43 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - ( $p$  - aminoanilide)], 4.55 parts of triethylamine and 160 parts of N - methylpyrrolidone was added under the same conditions. After reacting for several hours at room temperature, the viscous solution was pressure-filtered, the elastomer was precipitated with water, washed and dried. 46 Parts of an elastomer having a content of oligoamide of about 18%, a relative viscosity  $\eta$  rel. of 1.6, determined on a solution of 1 g of product in 100 ml of  $\sigma$ -chlorophenol at 20°C, and a softening point of about 230°C were obtained.

## EXAMPLE 9

25.33 Parts of a copolyether of tetrahydrofuran and epichlorhydrin having a chlorine content of 17.1% and an average molecular weight of 1490 were dissolved in 110 parts of N - methylpyrrolidone. 20 Parts of solvent were distilled off. After the addition of 3.78 parts of absolute triethylamine the solution was added dropwise within 20 minutes, while cooling with ice, to a soluton of 9.47 parts of sebacinyl chloride in 30 parts of chlorobenzene. The temperature was kept for 6 hours below +5°C and then a second solution of 8.9 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - ( $p$  - aminoanilide)], 5.7 parts of triethylamine and 170 parts of N-methylpyrrolidone was added within 20 minutes. The batch was kept for 10 hours at a temperature below +10°C and then pressure-filtered. A slight excess amount of triethylamine and the bulk of the chlorobenzene were distilled off under strongly reduced pressure at as low a temperature as possible. The product was precipitated with water, washed and dried. 39.5 Parts of an elastomer having a content of oligoamide of 22%, a chlorine content of 10.5%, a relative viscosity of 1.7, determined on a solution of 1 g of substance in 100 ml of  $\sigma$ -chlorophenol at 20°C, and a softening point of about 220°C were obtained.

## EXAMPLE 10

17.34 Parts of a poly - 1,2 - butylene oxide glycol of an average molecular weight of 2020 were dissolved in 90 parts of N-methylpyrrolidone. 20 Parts of solvent were distilled off under reduced pressure to remove moisture. After the addition of 3.44 parts of absolute triethylamine the solution was added within 20 minutes, while cooling with ice, to a solution of 11.0 parts of sebacinyl chloride in 35 parts of anhydrous chlorobenzene. After reacting for 4 hours at room temperature, a second solution of 11.38 parts of N,N' - terephthaloyl - bis - ( $\beta$  - aminoisovaleric acid hydrazide) of the formula



(obtained from N,N' - terephthaloyl - bis - (4,4 - dimethyl - azetidine - 2 - one) and hydrazine hydrate in excess, melting point after crystallization from water 263°C), 6.6 parts of triethylamine and 100 parts of N-methylpyrrolidone was added within 20 minutes while cooling with ice. The batch was allowed to stand overnight at room temperature and was then pressure-filtered and precipitated with water after removal of the chlorobenzene. The colourless rubber-like product was thoroughly washed with water and then dried at 60°C in a vacuum dryer. 34 Parts of an elastomer having a content of oligoamide of about 31%, a relative viscosity  $\eta$  rel. of 2.3, determined on a solution of 1 g of substance in 100 ml of  $\sigma$ -chlorophenol at 20°C, and a softening point of about 200°C. Filaments spun into water for a 50% solution in dimethylformamide had an elongation at break of 400%, an elastic recovery of 80% at an elongation of 100%, and a tensile strength of 0.45 g/den.

## EXAMPLE 11

32.8 Parts of a copolyester of adipic acid and ethylene glycol/propylene - 1,2-glycol (1:1) having a content of hydroxyl groups of 1.77% and an acid number of 1.5 were dissolved in 120 parts of N - methylpyrrolidone. From the solution 20 parts of solvent were distilled off, 3.44 parts of pure triethylamine were added and after cooling the total solution was added dropwise within 20 minutes, while cooling with

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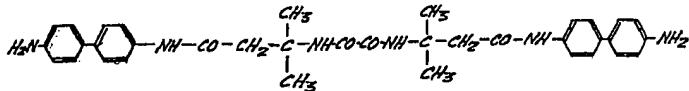
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ice, to 8.6 parts of sebacic acid chloride. After reacting for 4 hours at 10 to 15°C a second solution of 11.79 parts of N,N' - oxalyl - bis - [β - aminoisovaleric acid - 4-(4' - amino - diphenyl) - amide] of the formula



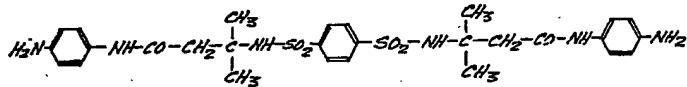
5 (obtained from N,N' - oxalyl - bis - (4,4 - dimethyl - azetidine - 2 - one) and at least 2 moles of benzidine, melting point after crystallization from pyridine 317°C), 170 parts of anhydrous N - methylpyrrolidone and 4.55 parts of absolute triethylamine was added within 20 minutes while cooling with ice. After reacting for 10 hours at room temperature, the viscous solution was pressure-filtered and the product was precipitated with water, washed and dried. 46 Parts of an elastomer having a relative viscosity  $\eta$  rel. of 1.8, determined on a solution of 1 g of product in 100 ml of o-chlorophenol at 20°C, and a softening point of about 230°C were obtained.

EXAMPLE 12

15 A solution of 40 parts of anhydrous polypropylene oxide glycol of an average molecular weight of 4000, 2.33 parts of absolute triethylamine and 140 parts of N - methylpyrrolidone was added dropwise at 15°C within 30 minutes to 7 parts of sebacinyl chloride. After reacting for 4 hours at room temperature a solution of 9.31 parts of N,N' - oxalyl - bis - β - aminoisovaleric acid - 4 - (4' - aminodiphenyl) - amide], 4 parts of triethylamine and 160 parts of N - methylpyrrolidone was added within 20 minutes. After 30 hours at room temperature, the elastomer was precipitated with water, washed and dried. 52 Parts of an elastomer having a relative viscosity  $\eta$  rel. of 1.9, determined on a solution of 1 g of product in 100 ml of o-chlorophenol at 20°C, and a softening point of about 230°C were obtained.

EXAMPLE 13

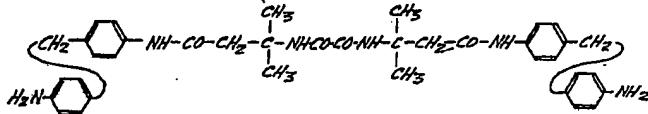
25 An anhydrous solution of 25.55 parts of a polypropylene oxide glycol of an average molecular weight of 2100, 3 parts of triethylamine and 100 parts of N - methylpyrrolidone was added dropwise within 20 minutes, while cooling with ice, to a solution of 8.6 parts of sebacinyl chloride in 30 parts of absolute dioxane. After 4 hours a second solution of 5.62 parts of N,N' - oxalyl - bis - [β - aminovaleric acid - (p - aminonanilide)], 3.63 parts of N,N' - benzene - 1,4 - disulfonyl - bis - [β - aminoisovaleric acid - (p - aminoanilide)] of the formula



35 (obtained from N,N' - benzene - 1,4 - disulfonyl - bis - [4,4 - dimethyl - azetidine-2-one] and 2 moles of p-phenylenediamine, melting point after crystallization from dimethylformamide/methanol 259°C), 4.55 parts of triethylamine and 180 parts of N - methylpyrrolidone was added within 30 minutes at a temperature within the range of +5 to +15°C. The batch was stirred for about 20 hours at room temperature and the elastomer was precipitated or spun into water, if desired after pressure filtration. 39.5 Parts of an elastomer having a content of oligoamide of about 23%, a softening point of about 200°C and a relative viscosity  $\eta$  rel. of 2.4, determined on a solution of 1 g of elastomer in 100 ml of o - chlorophenol at 20°C. Filaments spun into water from a 40% solution in dimethylformamide had an elongation at break of 1100% and an elastic recovery of 90% at an elongation of 100%.

EXAMPLE 14

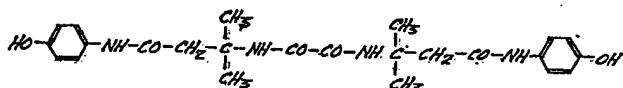
45 In the manner described in Example 13, a polyether containing terminal acid chloride groups was prepared by adding dropwise within 20 minutes, while cooling, an anhydrous solution of 29.48 parts of a polypropylene oxide glycol of a molecular weight of about 2100, 3.64 parts of triethylamine and 130 parts of N - methylpyrrolidone to a solution of 8.6 parts of sebacinyl chloride in 30 parts of absolute dioxane. The second solution consisted of 9.73 parts of N,N' - oxalyl - bis[β - aminoisovaleric acid - [4 - (4' - aminobenzyl) - anilide]] of the formula



(obtained from N,N' - oxalyl - bis - (4,4 - dimethyl - azetidine - 2 - one) and at least 2 moles of 4,4' - diaminodiphenylmethane, melting point after crystallization from acetonitrile 238°C), 4 parts of triethylamine and 120 parts of N - methylpyrrolidone. 44 Parts of an elastomer having a content of oligoamide of 22%, a softening point of about 190°C and a relative viscosity of  $\eta$  rel. of 1.8, determined on a solution of 1 g substance in 100 ml of o-chlorophenol at 20°C, were obtained. Filaments spun into water from a 50% solution in dimethylformamide had an elongation at break of 480% and an elastic recovery of 90% at an elongation of 100%.

## EXAMPLE 15

10 An anhydrous solution of 29.4 parts of a poly - 1,2 - butylene - oxide glycol of an average molecular weight of 2100, 3.6 parts of triethylamine and 110 parts of N-methylpyrrolidone was added dropwise within 20 minutes, while cooling with ice, to a solution of 9.56 parts of sebacinyl chloride in 30 parts of chlorobenzene and the batch was allowed to stand for 4 hours at room temperature. A second solution of 6.56 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - (p - aminoanilide)], 3.29 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - (p - hydroxy - anilide)] of the formula



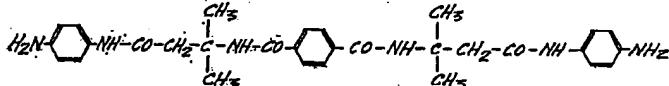
20 (obtained from N,N' - oxalyl - bis - [4,4 - dimethyl - azetidine - 2 - one] and 2 moles of p-aminophenol, melting point after crystallization from methanol 247°C), 5 parts of triethylamine and 180 parts of N - methylpyrrolidone was then added under the same conditions. After about 20 hours, the viscous solution was pressure-filtered, the chlorobenzene was removed and the elastomer was precipitated. 44 Parts of a block polymer having a content of oligoamide of about 22%, a softening point of 210°C and a relative viscosity of  $\eta$  rel. of 1.6, determined on a solution of 1 g of substance in 100 ml of o-chlorophenol at 20°C were obtained.

## EXAMPLE 16

30 To a solution of 10 parts of sebacic acid chloride in 20 parts of dioxane an anhydrous solution of 29.4 parts of a poly - 1,2 - butylene oxide glycol of a molecular weight of about 2100, 2.3 parts of pyridine and 110 parts of dimethylformamide was added within 20 minutes at 0 to +5°C and the batch was kept for 4 hours at the said temperature. After that time, a solution of 5.15 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - (p - aminoanilide)], 5.15 parts of N,N' - oxalyl - bis - [ $\beta$  - aminoisovaleric acid - (m - aminoanilide)], 4 parts of pyridine and 200 parts of dimethylformamide was added within 20 minutes while continuing cooling. A clear solution which became rapidly viscous was obtained. The batch was allowed to stand overnight at room temperature and the elastomer was then precipitated with water. 45 Parts of an elastomer having a content of oligoamide of about 22.5%, a softening point of about 180°C and a relative viscosity  $\eta$  rel. of 1.5, determined on a solution of 1 g of product in 100 ml of o-chlorophenol at 20°C were obtained. In the system N - methylpyrrolidone/triethylamine, a product of a relative viscosity  $\eta$  rel. of 1.9 was obtained. Filaments spun into water from a 50% solution in dimethyl - formamide had an elongation at break of 420% and an elastic recovery of 90% at an elongation of 100%.

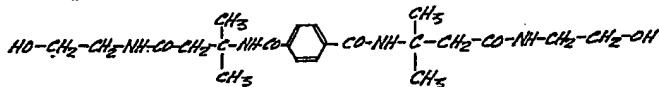
## EXAMPLE 17

45 19.8 Parts of a copolyester of adipic acid, ethylene glycol and diethylene glycol having a content of hydroxyl groups of 1.61% and an acid number smaller than 1.5 and 11.34 parts of a copolyether of tetrahydrofuran and propylene oxide in a ratio of 1:1 of an average molecular weight of 1260 were dissolved in 130 parts of N-methylpyrrolidone and 20 parts of solvent were distilled off to remove moisture. After the addition of 4.55 parts of absolute triethylamine the solution was added dropwise within 20 minutes, while cooling with ice, to a solution of 10 parts of sebacinyl chloride in 35 parts of absolute tetrahydrofuran. The batch was stirred for 4 hours at room temperature and a solution of 9.8 parts of N,N' - terephthaloyl - bis - [ $\beta$  - aminoisovaleric acid - (p - aminoanilide)] of the formula



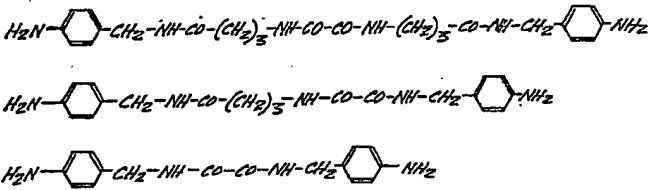
(obtained from 1 mole of N,N' - terephthaloyl - bis - (4,4 - dimethyl - azetidine - 2 - one) and 2 moles of *p*-phenylenediamine, melting point after crystallization from dimethylformamide/methanol 297°C), 170 parts of anhydrous N - methylpyrrolidone and 4.55 parts of absolute triethylamine was then added under the same conditions. After some hours the viscous solution was pressure-filtered and the product was precipitated with water, washed and dried. 47 Parts of an elastomer having a content of oligoamide of 21%, a softening point of about 220°C and a relative viscosity  $\eta$  rel. of 1.9, determined on a solution of 1 g of substance in 100 ml of *o*-chlorophenol at 20°C, were obtained.

**EXAMPLE 18**  
In the manner described in the preceding Examples a polyether containing terminal acid chloride groups was obtained by adding within 20 minutes, while cooling with ice, an anhydrous solution of 34.65 parts of poly - 1,2 - butylene oxide glycol of a molecular weight of 2100, 130 parts of N - methyl - pyrrolidone - (2) and 4 parts of triethylamine to a solution of 10.4 parts of sebacinyl chloride in 35 parts of chlorobenzene. The second solution consisted of 8.07 parts of N,N' - oxaryl - bis - [ $\beta$ -aminoisovaleric acid - 4(4' - aminodiphenyl) - amide], 2.93 parts of N,N' - terephthaloyl - bis - [ $\beta$  - aminoisovaleric acid - ( $\beta$  - hydroxyethylamide)] of the formula



(obtained from N,N' - terephthaloyl - bis - (4,4 - dimethyl - azetidine - 2 - one) and 2 moles of ethanolamine (melting point after crystallization from water 209°C), 120 parts of N - methylpyrrolidone - (2) and 5 parts of triethylamine, 51.1 Parts of an elastomer having a content of oligoamide of about 21%, a softening point of about 220°C and a relative viscosity  $\eta$  rel. of 1.2, determined on a solution of 1 g of substance in 100 ml of *o*-chlorophenol at 20°C, were obtained.

**EXAMPLE 19**  
A polyether containing terminal acid chloride groups was prepared by adding within 20 minutes at +10°C an anhydrous solution of 31.05 parts of poly - 1,2-butylene oxide glycol of a molecular weight of about 2100, 3.54 parts of triethylamine and 100 parts of N - methylpyrrolidone - (2) to 11 parts of sebacinyl chloride. The mixture was heated for 4 hours at 40°C. Then an anhydrous solution of 130 parts of N - methylpyrrolidone - (2), 5.6 parts of triethylamine and 9 parts of the reaction product of N,N' - oxaryl - bis - pyrrolidone - (2) and *p* - aminobenzylamine was added at +10°C. The said reaction product obtained at room temperature from 1 mole of N,N' - oxaryl - bis - pyrrolidone - (2) and 2 moles of *p* - aminobenzylamine in dimethylformamide was a mixture of the following three diaminoamides:



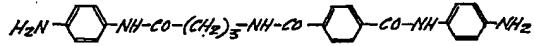
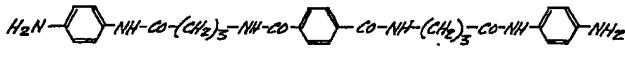
The mixture contained 18.6% of total nitrogen and 7.78% of basic nitrogen and had an average molecular weight of 360 and a solidification point of 166 to 169°C.

After reacting for 20 hours at room temperature in one instance and, in another instance, for 5 hours at 50°C, the viscous solution was pressure-filtered, the elastomer was precipitated with water and dried. 47 Parts of a polymer having a content of oligoamide of about 19%, a softening point of about 240°C and a relative viscosity  $\eta$  rel. of 2.1, determined on a solution of 1 g of product in 100 ml of *o*-chlorophenol at 20°C, were obtained. The elastomer was wet spun from N-methylpyrrolidone.

**EXAMPLE 20**  
A polyether containing terminal acid chloride groups was obtained by adding within 20 minutes at +10°C an anhydrous solution of 29.4 parts of poly - 1,2-butylene oxide glycol of a molecular weight of about 2100, 3.24 parts of triethylamine and 80 parts of N - methylpyrrolidone - (2) to 10 parts of sebacinyl chloride. The batch was heated at 40°C for 4 hours. After that time an anhydrous solution of

5        200 parts of N - methylpyrrolidone - (2), 5.06 parts of triethylamine, 5.15 parts of N,N' - oxaryl - bis - [ $\beta$  - aminoisovaleric acid - (m - amino - anilide)] and 4.02 parts of the reaction product of N,N' - terephthaloyl - bis - pyrrolidone - (2) and p - phenylenediamine was added at room temperature. The said reaction product which had been obtained from 1 mole of N,N' - terephthaloyl - bis - pyrrolidone - (2) and 2 moles of p - phenylenediamine in dimethylformamide at 120°C, was a mixture of the following three diaminoamides:

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10         $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{NH}-\text{C}_6\text{H}_4-\text{NH}_2$

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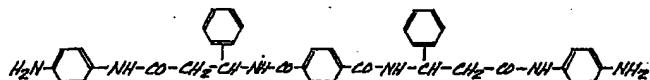
The mixture contained 16.1% of total nitrogen and 7.58% of basic nitrogen and had an average molecular weight of 370 and a decomposition point of 310 to 315°C. After reacting for 20 hours, the product was precipitated with water, washed and dried. 43 Parts of an elastomer having a content of oligoamide of about 20%, a softening point of about 260°C and a relative viscosity  $\eta$  rel. of 1.6, determined on a solution of 1 g of product in 100 ml of N - methylpyrrolidone at 20°C, were obtained. The product was wet spun from N-methylpyrrolidone.

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## EXAMPLE 21

20        An anhydrous solution of 18.63 parts of poly - 1,2 - butylene oxide glycol of a molecular weight of about 2100, 70 parts of N - methylpyrrolidone - (2) and 2 parts of triethylamine was added dropwise within 30 minutes at room temperature to 4.78 parts of sebacic acid chloride. The solution was heated for 3 hours at 50°C. Then a second solution of 80 parts of N - methylpyrrolidone - (2), 2.5 parts of triethylamine and 5.76 parts of N,N' - terephthaloyl - bis - [ $\beta$  - amino -  $\beta$  - phenyl - propionic acid - (p - aminoanilide)] of the formula

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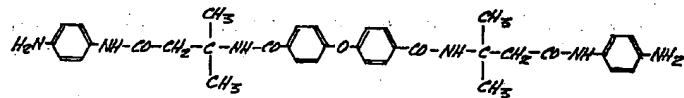
25        (obtained from 1 mole of N,N' - terephthaloyl - bis - (4 - phenylazetidine - 2 - one) and 2 moles of p - phenylenediamine, melting point after crystallization from dimethylformamide/methanol 326°C) was added at room temperature. After reacting for 15 hours at room temperature the viscous solution was pressure-filtered, the elastomer was precipitated with water and dried. 27 Parts of a product having a content of oligoamide of 21%, a softening point of above 260°C and a relative viscosity  $\eta$  rel. of 1.5, determined on a solution of 1 g of product in 100 ml of N - methylpyrrolidone at 20°C, were obtained. The elastomer could be spun from N-methylpyrrolidone.

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## EXAMPLE 22

30        An anhydrous solution of 20.2 parts of poly - 1,2 - butylene oxide glycol, 80 parts of N - methylpyrrolidone - (2) and 2.2 parts of triethylamine was added dropwise at + 20°C within 20 minutes to 9.56 parts of sebacinyl chloride. The solution was heated at 40°C for 4 hours. Then a second solution of 140 parts of N - methylpyrrolidone - (2), 6.1 parts of triethylamine, 8 parts of N,N' - terephthaloyl - bis - ( $\beta$  - amino - isovaleric acid hydrazide) and 2.3 parts of N,N' - (diphenyl ether - 4,4' - dicarboxyl) - bis - [ $\beta$  - aminoisovaleric acid - (4 - aminoanilide)] of the formula

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35        (obtained from 1 mole of N,N' - (diphenyl ether - 4,4' - dicarboxyl) - bis - (4,4 - dimethyl - azetidine - 2 - one) (melting point 160°C) and 2 moles of p - phenylenediamine, melting point after crystallization from dimethylformamide/ether 250°C), was added at + 20°C.

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40        After reacting for 20 hours at room temperature, the viscous solution was pressure-filtered, the product was precipitated with water, washed and dried. 37 Parts of

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an elastomer having a content of oligoamide of about 29.7%, a softening point of about 160°C and a relative viscosity  $\eta$  rel. of 1.9, determined on a solution of 1 g of product in 100 ml of o-chlorophenol at 20°C, were obtained. The elastomer could be spun into water from a 47% solution in dimethyl-formamide.

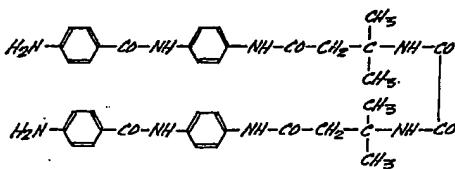
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## EXAMPLE 23

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In a kneader provided with cooling means 4.26 parts of azelaic acid dichloride were placed. At a temperature of +5°C an anhydrous solution of 20.8 parts of a polyester of adipic acid, ethylene glycol and diethylene glycol (molar ratio 1:1) having a content of hydroxyl groups of 1.62% and an acid number of 1.28, 2.2 parts of triethylamine and 25 parts of N - methyl - pyrrolidone - (2) was added within 30 minutes. After reacting for 4 hours at room temperature, 6.36 parts of N,N' - oxalyl-bis - { $\beta$  - amino - isovaleric acid - [N'' - (4' - aminobenzoyl) - 4 - aminoanilide]} of the formula

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(obtained from 1 mole of N,N' - oxalyl - bis - (4,4 - dimethyl - azetidine - 2 - one) and 2 moles of N - (4 - aminobenzoyl) - p - phenylenediamine, melting point after crystallization from dimethylformamide/methanol 327°C) were sprinkled in a solid form and admixed by kneading and then 2.53 parts of triethylamine were added dropwise within 20 minutes while cooling. After kneading for 6 hours, the product was washed with water and dried. 30 Parts of an elastomer having a content of oligoamide of 21%, a softening point of about 270°C and a relative viscosity  $\eta$  rel. of 2.4, determined on a solution of 1 g of product in 100 ml of o-chlorophenol at 20°C were obtained. Filaments spun into water from a 33% solution in dimethylformamide had an elongation at break of 700%, an elastic recovery of 95% at an elongation of 100% and a tensile strength of 0.5 g/den.

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## WHAT WE CLAIM IS: —

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1. A process for the manufacture of an elastomeric block co-polymer which comprises treating, in the presence of an acid-binding substance, a polyether and/or a polyester dicarboxylic acid halide or disulphonic acid halide having an average molecular weight in the range of from 500 to 5000 and a softening point less than 60°C, if desired together with up to 400 mol %, based on the amount of the acid halide or halides, of a simple dicarboxylic acid halide, with from 10 to 50% by weight calculated on the total weight of the reactants of an oligoamide having a molecular weight of at least 230 and containing a terminal group capable of being acylated.

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2. A process as claimed in claim 1 carried out in solution.

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3. A process as claimed in claim 2, wherein the solvent is chlorobenzene, dioxane, acetonitrile, dimethylformamide, dimethylacetamide, phosphoric acid - tris - dimethylamide, N - methylpyrrolidone or a mixture of any two or more of these substances.

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4. A process as claimed in any one of claims 1 to 3, carried out at a temperature in the range of from -20 to +80°C.

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5. A process as claimed in claim 4, wherein the temperature is in the range of from 0 to 30°C.

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6. A process as claimed in any one of claims 1 to 5, wherein a polyether and/or a polyester dicarboxylic acid halide is used and wherein the polyether and/or the polyester dicarboxylic acid halide has been prepared by the reaction between a polyether and/or a polyester containing a terminal hydroxy group and from 1 to 2 moles of a dicarboxylic acid halide or phosgene.

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7. A process as claimed in any one of claims 1 to 5, wherein a polyether and/or a polyester dicarboxylic acid halide is used and wherein the polyether and/or the polyester dicarboxylic acid halide has been prepared by the reaction between a polyether and/or a polyester containing a terminal hydroxyl group with at least 2 mols of a dicarboxylic acid halide or phosgene.

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8. A process as claimed in claim 6 or 7, wherein the dicarboxylic acid halide is sebacic acid halide.

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9. A process as claimed in any one of claims 1 to 5 wherein a polyether and/or a polyester disulphonic acid halide is used and wherein the polyether and/or the poly-

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- ester disulphonic acid halide has been prepared by the reaction between a polyether and/or a polyester containing a terminal hydroxyl group with from 1 to 2 moles of a disulphonic acid halide.
10. A process as claimed in any one of claims 1 to 5, wherein a polyether and/or a polyester disulphonic acid halide is used and wherein the polyether and/or the polyester disulphonic acid halide has been prepared by the reaction between a polyether and/or a polyester containing a terminal hydroxyl group with at least 2 moles of a disulphonic acid halide. 5
11. A process as claimed in any one of claims 1 to 5, wherein a polyether and/or a polyester dicarboxylic or sulphonic acid halide is used which has been prepared from a polyether and/or a polyester containing a terminal carboxylic acid or sulphonic acid group and a halogenating compound. 10
12. A process as claimed in claim 11, wherein the halogenating compound is phosphogene, thionyl chloride, phosphorus oxychloride, phosphorus pentachloride, phosphorus trichloride or a bromide corresponding to any of the aforementioned chlorides. 15
13. A process as claimed in any one of claims 1 to 12, wherein a polyether dicarboxylic or disulphonic acid halide is used and wherein the polyether is a copolymer. 15
14. A process as claimed in any one of claims 1 to 13, wherein a polyether dicarboxylic or disulphonic acid halide is used and at least some of the oxygen atoms in the polyether have been replaced by sulphur atoms. 20
15. A process as claimed in any one of claims 1 to 14, wherein a polyester dicarboxylic or disulphonic acid halide is used and the polyester is a copolyester. 20
16. A process as claimed in claim 15, wherein the copolyester is a copolyester of adipic acid, ethylene glycol and 1,3 - butanediol of adipic acid, phthalic acid and ethylene glycol or of terephthalic acid, ethylene glycol and polyethylene oxide glycol. 25
17. A process as claimed in any one of claims 1 to 16, wherein the oligoamide is the product of a transamidation reaction between a N,N' - acyl - bis - lactam or a derivative thereof and a compound capable of being bis-acylated in which one of the groups capable of being acylated is a primary or secondary amino group. 30
18. A process as claimed in claim 17, wherein a N,N' - acyl - bis -  $\beta$  - lactam or a derivative thereof is used. 30
19. A process as claimed in claim 18 wherein N,N' - oxalyl - bis(4,4 - dimethylazetidine - 2 - one), N,N' - terephthaloyl - bis - pyrrolidone - 2 or 4,4' - dimethylazetidinone is used. 35
20. A process as claimed in any one of claims 17 to 19 wherein the compound capable of being bis-acylated is one of the compounds hereinbefore described. 35
21. A process as claimed in any one of claims 1 to 20, wherein as acid-binding substance a tertiary organic amine is used. 40
22. A process as claimed in any one of claims 1 to 20, wherein as acid-binding substance there is used pyridine N - methyl - piperidine, N,N - dimethylaniline, triethylamine sodium hydroxide, sodium carbonate or magnesium oxide. 40
23. A process as claimed in claim 1 carried out substantially as described in any of the Examples herein. 45
24. An elastomeric block polymer whenever prepared by a process as claimed in any one of claims 1 to 22. 45
25. A filament, a fibre a sheet, a film or any other shaped structure which comprises an elastomeric block polymer as claimed in claim 23 or 24. 50
26. A lacquer a varnish, an adhesive or a thickening agent which comprises an elastomeric block polymer as claimed in claim 23 or 24. 50

ABEL & IMRAY,  
Chartered Patent Agents,  
Quality House, Quality Court, Chancery Lane, London, W.C.2.

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